

APPLICATION

of

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for

UNITED STATES LETTERS PATENT

on

MASTERBATCH

Client ID/Matter No. URQUH-67793

Sheets of Drawing Figures: 2 sheets

Express Mail Label No. EV 327058648 US

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MASTERBATCH

[0001] This is a continuation of International Application PCT/GB02/03644, with an international filing date of August 7, 2002, which claims priority from United Kingdom Application No. 0120985.7 filed on August 29, 2001, the contents of which are all hereby incorporated by reference in their entireties.

[0002] The present invention is concerned with a method of colouring thermoplastics, and in particular colouring PVC. The present invention is also concerned with a masterbatch for use in colouring thermoplastics, a method of making such a masterbatch, and a masterbatch carrier system for PVC.

[0003] In order to provide coloured thermoplastics it is known to colour a base thermoplastic (which is typically of a neutral colour) by the use of pigment packs and/or liquid colour concentrates, or using dry, typically pelletised, coloured concentrates known in the plastics industry as a masterbatch. Alternatively, the thermoplastic material is supplied as a coloured compound.

[0004] Masterbatches are typically produced in 2 types, namely Universal and Polymer specific. Universal masterbatches are general purpose masterbatches typically used at about 1 to 2% by weight LDR. The Universal masterbatch, as its name implies, is based on a universal carrier type in order to minimise the effects on a polymer it is used in.

[0005] However, known Universal masterbatches have a number of disadvantages which include lamination, a decrease in physical properties (for example reduction in impact strength, flexural modulus etc.) and difference in shrinkages.

[0006] Polymer specific masterbatches are based on the polymers that the concentrate is to be used in, and are typically used at about 1 to 5% by weight LDR. Whilst there appears to be little adverse reaction between the masterbatch carrier and the base polymer, Polymer specific masterbatches are disadvantageous as a separate masterbatch has to be formulated and manufactured for each polymer; thereby increasing the number of masterbatches produced and creating the requirement of additional storage by the actual manufacturers of the coloured

thermoplastics. Furthermore, each time a producer modifies the polymer, a different masterbatch has to be manufactured thereby rendering the old polymer specific masterbatch obsolete.

[0007] PVC (Polyvinylchloride) is an extremely versatile, commodity thermoplastic. Its mechanical properties can be easily adjusted to meet specific requirements of the end user. However, a main problem with the use of PVC is its low thermostability during processing. As PVC degrades, hydrogen chloride is given off which not only is undesirable in itself but also has a disadvantage of further accelerating the degradation of PVC.

[0008] The dehydrochlorination problem has resulted in PVC being unpopular with a large section of the thermoplastics processing industry. The industry therefore tends to be split into processors who base their business on PVC and those whose base their businesses on all polymers except PVC.

[0009] There are two types of PVC, plasticised or flexible PVC (PVC), and unplasticised or rigid PVC (PVCu).

[00010] Plasticised or flexible PVC is generally produced as a coloured compound, it can be masterbatched using 1 to 2% by weight Universal masterbatch, or 2 to 5% by weight flexible PVC-based masterbatch.

[00011] Unplasticised or rigid PVC is almost always produced as a coloured compound. However it is possible to be mass coloured using a Universal masterbatch (which is typically unpredictable to the success of the end product), or using a flexible PVC masterbatch which is disadvantageous as it incorporates a plasticiser into a material which is selected for its unplasticised nature.

[00012] The production of coloured PVC (plasticised or unplasticised) is undesirable as large quantities of each individual colour has to be produced by the manufacturer and therefore stored by the end user. Masterbatches are advantageous as the neutral coloured PVC can be produced on mass and subsequently coloured, typically using, up to about 6% of the masterbatch.

[00013] As mentioned hitherto before, the main problem with colouring PVC by the masterbatch route is due to the low thermostability of PVC. In addition, as a result of this low

thermostability, processing of PVC tends to be low shear, so as to not subject the polymer to localised overheating due to the creation of frictional heat. Masterbatches rely on being "worked" to wet out into the polymer and homogenise the compound. This working is not a problem for more stable thermoplastics. Typical pigment loading for masterbatches are 20 - 70% and it is very difficult to subject a PVC compound to the amount of shear required to incorporate pigments at these levels.

[00014] It is therefore an aim of the present invention to alleviate at least some of the problems identified above.

[00015] It is a further aim of the present invention to provide a multi-purpose masterbatch for use in colouring PVC (in particular PVCu).

[00016] It is yet a further aim of the present invention to provide a method of making a masterbatch suitable for use in colouring thermoplastics.

[00017] According to yet a further aim of the present invention, there is provided a method of manufacturing a masterbatch; the masterbatch being suitable for use in the colouring of thermoplastics.

[00018] It is yet a further aim of the present invention to provide a formulation for use in introducing performance enhancing additives to PVC.

[00019] According to the present invention, there is therefore provided a multi-purpose masterbatch carrier which includes:

a chlorinated polyolefin;

an acrylic processing aid; and

an acrylic impact modifier.

[00020] The carrier is preferably for use with dyes, pigments, functional additives or the like, which may, for example, be added to the masterbatch when the masterbatch is being manufactured.

[00021] The present invention further extends to a masterbatch which includes:

- a chlorinated polyolefin;
- a acrylic processing aid;
- an acrylic impact modifier; and
- at least one dye, pigment or functional additive.

[00022] The masterbatch may further include processing additives, incidental ingredients, fillers and/or impurities.

[00023] A functional additive is an additive which is beneficial to the end PVC product. Functional additives may include UV stabilisers, anti-stats, flame retardants or the like.

[00024] A processing aid for PVC is a thermoplastic resin added to the PVC compound in relatively small quantities in order to improve its processing characteristics on the way from the raw material to the semifinished and finished article.

[00025] Processing aids advantageously possess one or more of the following properties:

- acceleration of the melting process
- improvement of the rheological properties in the thermoplastic state
- improvement of the mechanical properties in the thermoelastic state

[00026] An impact modifier for PVC is a material that when incorporated into a naturally brittle material (eg PVCu) converts it to one of high toughness (where the tensile strength of the material is equal or higher than its yield stress).

[00027] The masterbatch may further include one or more additives including calcium oxide (typically present in an amount 4.0 to 6.0% by weight of the masterbatch), calcium stearate (typically present in an amount 1.5 to 6.0% by weight of the masterbatch), chalk (typically present in an amount 0.0 to 30.0% by weight of the masterbatch), a wax, such as amide wax,

polyethylene wax oxidised or unoxidised, or montan wax (the wax is preferably present in an amount 0% to 10% by weight of the masterbatch).

[00028] Advantageously, when the masterbatch according to the present invention is used to colour PVC, the resultant coloured PVC compound does not contain ingredients which would be detrimental to the coloured PVC compound.

[00029] Preferably, the chlorinated polyolefin is present in an amount up to about 30% by weight of the total weight of the masterbatch. Further preferably, the chlorinated polyolefin is present in an amount up to 25% by weight of the total weight of the masterbatch.

[00030] The chlorinated polyolefin may include a chlorinated polyester elastomer, chlorinated polyethylene or chlorinated polypropylene although chlorinated polyethylene is preferred. Typically the chlorine content of the polyolefin should be greater than 30. The crystallinity (DS) of the chlorinated polyolefin may vary from about 0 to about 1.0, although it is preferred crystallinity is about 0.7.

[00031] The shore A hardness of the chlorinated polyolefin is preferably no more than about 95, typically no more than about 65.

[00032] The acrylic processing aid may be present in an amount up to about 10% by weight of the masterbatch. However, it is preferred that the acrylic processing aid is present in an amount up to about 5% by weight of the masterbatch.

[00033] Preferred acrylic processing aids include a methyl-methacrylate based processing aids, although other suitable acrylic processing aids may be included. The methyl methacrylate based processing aids are typically co-polymerised with ethyl acrylate (EA), Butyl acrylate (BA), Butyl methylacrylate (BMA) or styrene. A particularly preferred processing aid includes a polymethyl methacrylate based processing aid, such as the type commercially available as Reamod P220 or Reamod P270.

[00034] Methyl methacrylate based processing aids are preferred as they have:

- no or a retarding influence on the melting process

- no influence on the viscosity of the PVC melt
- moderate die swell
- moderate adhesion to metal
- favourable influence on thermoforming behaviour

[00035] The acrylic impact modifier is preferably present in an amount up to about 30% by weight of the masterbatch, further preferably in an amount up to about 25% by weight of the masterbatch.

[00036] The acrylic impact modifier may be an acrylic/styrene polymer. Alternatively poly (BA/MMA) or poly(EA/MMA) may be used. A preferred impact modifier includes Paraloid HIA80 or Paraloid KM 355. It is, however, envisaged that ABS and MBS may be used in the present invention.

[00037] The use of polyacrylates as the impact modifier are particularly advantageous as they have the following properties:

- trouble free processing
- high light and weathering resistance
- high level of notched impact strength achievable
- good surface formation
- high aging resistance

[00038] The dye and/or pigment may be any standard dye/pigment used in the colouring of thermoplastics.

[00039] The ratio of the amounts of the chlorinated polyolefin, acrylic processing aid, acrylic impact modifier and the dye or pigment may be varied depending on the pigments and/or dye used, and also the concentration required and the end use of the masterbatch.

[00040] The present invention has a further advantage in the thermoplastics industry, as the masterbatch according to the invention has the advantage that additional processing aids (which reduce fusion time, increase lubrication and stabilise melt flow) and impact modifiers (which

reduce brittleness) do not need to be further added to the thermoplastic coloured with the masterbatch according to the invention. Furthermore, the acrylic processing and the impact modifier have the advantage of improving the gloss of the resultant coloured PVC.

[00041] Accordingly, there is further provided an additive for use in PVC processing, which comprises a blend of, at least, a chlorinated polyolefin, an acrylic processing aid and an acrylic impact modifier. The chlorinated polyolefin, the acrylic processing aid and the acrylic impact modifier are substantially as described hereinbefore.

[00042] According to a further aspect of the present invention, there is provided a method of manufacturing a masterbatch carrier, which method includes:

- a) blending at least one chlorinated polyolefin, at least one acrylic processing aid at least one acrylic impact modifier; and
- b) forming the blend into a shaped body.

[00043] According to yet a further aspect of the present invention there is provided a method of manufacturing a masterbatch suitable for use in the colouring of PVC (in particular PVCu), which method includes:

- a) blending at least one chlorinated polyolefin, at least one acrylic processing aid, at least one acrylic impact modifier and a pigment and/or dye; and
- b) forming the blend into a shaped body.

[00044] The chlorinated polyolefin, the acrylic processing aid and the acrylic impact modifier are substantially as described herein before.

[00045] The blending in step (a) is typically in a high speed high shear mixer, such as a Henschel, a TK Fielder or a Papenmeir mixer. The temperature during step (a) typically raises above ambient temperature. The elevated temperature is typically attained by frictional heat of the components of the blend. However, it is envisaged that a heating means may be utilised in order to increase the temperature if required. It is preferred that the temperature is controlled so as to remain substantially below about 80°C, preferably below about 70°C.

[00046] It is preferred that a process oil (such as white mineral oil, such as Presol 120) is added during step (a). The addition of the process oil advantageously dampens the blend, thereby aiding fusion of the components in step (a) and also assists in the formation of the shaped body in step (b) by, for example, extrusion. The process oil therefore acts as a lubricant.

[00047] The blending is typically carried out at a temperature in the range of from ambient to about 80°C, such as 70°C.

[00048] The chlorinated polyolefin, the acrylic processing aid and the acrylic impact modifier are all preferably free flowing powders, typically having a particle size of less than about 1200 μ (preferably less than about 700 μ) in diameter.

[00049] The additives (if present) and the dye and/or pigment typically have a particle size of less than about 1200 μ in diameter, although it is envisaged that the particle size may be less than about 100 μ in diameter (or less).

[00050] Preferably the chlorinated polyolefin, the acrylic modifier and the process oil (if present) are preblended prior to step (a). The preblending may be in the same vessel used for the blending in step (a), however, it is envisaged that a different vessel may be used.

[00051] The preblending may be for up to about 1 minute, however, it is preferred that the preblending is for up to about 20 seconds.

[00052] The resultant blend of chlorinated polyolefin, acrylic modifier and process oil (if present) achieved in the preblend is subsequently blended with the remaining components of the blend in step (a). The blend in step (a) may be for up to about 30 minutes, preferably up to about 20 minutes.

[00053] The temperature achieved during step (a) and/or step (b) may be up to about 70 to 80°C. However, it will be apparent to a person skilled in the art that the temperature achieved and/or the blending time in step (a) is dependent on the ingredients.

[00054] The forming in step (b) is typically by extrusion, using for example a co-rotating twin screw extruder. The extrusion is preferably carried out on an extruder configured with at least two mixing zones and/or at least eight temperature zones.

[00055] The extrusion temperature may be up to about 190°C. Although the temperature is typically in the range 125 to 140°C, averaging at about 135°C.

[00056] The blend may develop frictional heat whilst in the extruder. If the temperature rises over about 200°C the blend may degrade. It is therefore preferred that the temperature of the blend in step (b) is controlled, using for example, external cooling means.

[00057] Following extrusion the formed product is typically in the form of elongate strands (typically having a diameter of about 1-2mm). The elongate strands are subsequently pelletised using methods known in the art of forming pellets by extrusion or the like.

[00058] According to yet a further aspect of the present invention, there is provided a method of colouring PVC (in particular a PVCu), which method includes blending a masterbatch manufactured according to the present invention with a base PVC material.

[00059] The masterbatch is typically blended with the PVC material in a ratio in the range 1:100 to 1:10 masterbatch to base PVC material.

[00060] The present invention will be illustrated, by way of example only, with reference to the accompanying drawings, wherein;

[00061] FIGURE 1 is a flow chart showing an exemplary sequence of operations in the method according to the invention; and

[00062] FIGURE 2 is a flow chart showing an exemplary extruder arrangement.

[00063] Referring to the flow chart in Figure 1, the chlorinated polyolefin and the acrylic modifier are weighed and loaded into HSM (Block A). Prewighed process oil (if present) is subsequently added (Block B). The components are mixed, typically for about 5 seconds (Block C) before adding the remaining components (Block D). The components are then mixed for about 20 minutes (Block E) or mixed until the desired temperature of the homogenised

components is achieved (normally between 50 - 75°C)(Block F). The blended components are decanted to a day-bin (Block G).

[00064] The contents of the day-bin are emptied into extruder feed hopper (H), extruder feed screws are started (not to exceed about 600rpm) and the feed hopper started (Block I). Resulting extrudate is fed from the die (Block J) through the water bath and then drier (Block K) and into a pelletiser.

[00065] Referring to the flow chart in Figure 2, the feed hopper (Block L) receives the contents of the day-bin. The blended components pass through a series of controlled temperature zones (T1, T2, T3, T4, T5, T6, T7 and T8). Temperature zones T1 to T7 being controlled at about 140°C and T8 being controlled at about 110 - 120°C. After passing through the controlled temperature zones the blend enters a transition zone (Block M) which is controlled at a temperature of about 140°C and to spaghetti die (Block N) which produces the strands of blend.

[00066] The following examples are further illustrative of the present invention.

[00067] Example 1

[00068] The following ingredients (all having a particle size of less than about 1200 μ) were added to the high speed mixer.

Ingredient	Weight	Weight %
Wax PN 909 (processing aid)	0.0200	2.0028
Paraloid KM355	0.2250	22.5315
Process Oil	0.0200	2.0028
Chlorinated low density polyethylene 3611P	0.9500	9.5133

[00069] The ingredients were blended for up to 15 seconds, typically about 5 seconds.

[00070] The following ingredients were subsequently added to the high speed mixer and blended for a further 15 minutes.

Ingredient	Weight	Weight %
Alum Low Odour	0.0380	3.8053
PL Gold 323	0.3000	30.0420
Yellow 83	0.0133	1.3318
Red 247:1	0.0023	0.2303
Chalk	0.0400	4.0056
Calcium Oxide	0.0500	5.0070
CA Stearate	0.0200	2.0028
Wax 10DS	0.0750	7.5105
F00088	0.1000	10.0140

[00071] The temperature of the mixer is controlled such that the temperature does not exceed about 85°C.

[00072] After blending the resultant blend is discharged to a day bin which is subsequently emptied into an extruder feed hopper. The extruder feed screws are started (not to exceed about 600rpm) and the feed hopper started.

[00073] The blended components pass through a series of continued temperature zones as described hereinbefore with reference to figure 2. After passing through the controlled temperature zones the blend enters a transition zone which is controlled at a temperature of about 140°C and subsequently to a spaghetti die which produces strands of the blend.

[00074] The strands are fed from the die through a water bath and into a pelletizer to form free flowing pellets

[00075] These pellets are then used to colour PVCu.

[00076] Example 2

[00077] The following ingredients were blended and a masterbatch prepared according to the method outlined in Example 1.

[00078] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ .

Ingredient	Weight	Weight %
Alum Low Odour	0.1000	10.0000
Chalk	0.2850	28.5000
Calcium Oxide	0.0500	5.0000
CA Stearate	0.0250	2.5000
Wax 10DS (processing aid) #	0.0750	7.5000
Paraloid KM355 #	0.1000	10.0000
Chlorinated low density polyethylene 3611P #	0.2500	25.0000
F00088	0.1000	10.0000
Process Oil 01 #	0.0150	1.5000

[00079] Example 3

[00080] The following ingredients were blended and a masterbatch prepared according to the method outlined in Example 1.

[00081] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ .

Ingredient	Weight	Weight %
TiO ₂	0.5500	54.9560
Blue U/M 08	0.0022	0.2198
Violet U/M 11	0.0066	0.6594
Calcium Oxide	0.0500	4.9960
CA Stearate	0.0200	1.9984
Wax PN.909 #	0.0200	1.9984
Wax 10DS	0.0600	5.9952
Paraloid KM355 #	0.0900	8.9928
Chlorinated low density polyethylene 3611P #	0.2020	20.1838

[00082] Example 4

[00083] The following ingredients were blended and a masterbatch prepared according to the method outlined in Example 1 so as to provide a masterbatch having a magenta colour.

[00084] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ .

Ingredient	Weight	Weight %
Red 122	0.0300	3.0000
Blue U/M 08	0.0060	0.6000
Barytes	0.4640	46.4000
Calcium Oxide	0.0500	5.0000
CA Stearate	0.0250	2.5000
Wax E #	0.0750	7.5000
Paraloid KM355 #	0.1100	11.0000
Chlorinated low density polyethylene 3611P #	0.2400	24.0000

[00085] Example 5

[00086] The following ingredients were blended and a masterbatch prepared according to the method outlined in Example 1.

[00087] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ .

Ingredient	Weight	Weight %
Pearl 1000/Pearl 5000	0.1100	10.9945
Optical	0.0055	0.5497
Barytes	0.2350	23.4882
Calcium Oxide	0.0500	4.9975
CA Stearate	0.0500	4.9975
Wax PN.909 #	0.0500	4.9975
Wax OP		
Paraloid HIA80 #	0.2500	24.9875
Chlorinated low density polyethylene 3611P #	0.2500	24.9875

[00088] Approx 1 minute before the end of the mixing the following was added so as to provide a frost sparkle colour masterbatch.

Ingredient	Weight	Weight %
Pearl 1000/Pearl 5000	0.1100	10.9945

[00089] Example 6

[00090] The following ingredients were blended and a masterbatch prepared according to the method outlined in Example 1.

[00091] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ .

Ingredient	Weight	Weight %
Blue 15.3	0.0100	1.0000
Barytes	0.3350	33.5000
Calcium Oxide	0.0500	5.0000
Wax PN.909 #	0.0200	2.0000
CA Stearate	0.0300	3.0000
Wax OP	0.0500	5.0000
Paraloid HIA80 #	0.2500	25.0000
Chlorinated low density polyethylene 3611P #	0.2500	25.0000
Process Oil 01 #	0.0050	0.5000

[00092] Example 7

[00093] The following ingredients were blended and a masterbatch carrier system prepared according to the method outlined in Example 1.

[00094] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ

Ingredient	Weight	Weight %
Chalk	0.4800	48.0000
Calcium Oxide	0.0500	5.0000
Calcium Stearate	0.0250	2.5000
Wax PN 909 #	0.0200	2.0000
Wax E	0.0750	7.5000
Paraloid KM355 #	0.1100	11.0000
Chlorinated low density polyethylene 3611P #	0.2400	24.0000

[00095] The resultant carrier was suitable for use in the processing of PVC.

[00096] Example 8

[00097] The following ingredients were blended and a masterbatch carrier system an additive prepared according to the method outlined in Example 1.

[00098] The ingredients preblended are identified by #. All of the ingredients are in particulate from having a diameter less than about 1500 μ

Ingredient	Weight	Weight %
Barytes	0.3500	35.0000
Calcium Oxide	0.0500	5.0000
Calcium Stearate	0.0500	5.0000
Wax OP #	0.0500	5.0000
Paraloid HIA 80 #	0.2500	25.0000
Chlorinated low density polyethylene 3611P #	0.2500	25.0000

[00099] The resultant carrier was suitable for use in the processing of PVC.

[000100] Example 9

[000101] The following ingredients were blended and a masterbatch carrier system prepared according to the method outlined in Example 1.

[000102] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ

Ingredient	Weight	Weight %
Chalk	0.4650	46.5000
Calcium Oxide	0.0500	5.0000
Calcium Stearate	0.0250	2.5000
Wax PN909 #	0.0200	2.0000
PE Wax	0.0200	2.0000
Wax E	0.0600	6.0000
Paraloid P270 #	0.0275	2.7500
Paraloid KM355 #	0.0825	8.2500
Chlorinated low density polyethylene 36611P #	0.2400	24.0000
Process oil #	0.0100	1.0000

[000103] The resultant carrier was suitable for use in the processing of PVC.

[000104] Example 10

[000105] The following ingredients were blended and a masterbatch carrier system prepared according to the method outlined in Example 1.

[000106] The ingredients preblended are identified by #. All of the ingredients are in particulate form having a diameter less than about 1500 μ

Ingredient	Weight	Weight %
Chalk	0.4700	47.9591
Calcium Oxide	0.0500	5.1020
Calcium Stearate	0.0200	2.0408
Wax PN909	0.0200	2.0408
Wax E	0.0600	6.1224
Paraloid KM355	0.1580	16.1224
Chlorinated low density polyethylene 3611p #	0.1920	19.5918
Process Oil #	0.0100	1.0204

[000107] The resultant carrier was suitable for use in the processing of PVC.